IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants	:	Y. IKEMATSU et al.
Serial No.	:	10/552,668
Filed	:	October 5, 2005
For	:	HIGH STRENGTH MOLTEN ZINC PLATED STEEL SHEET AND PROCESS OF PRODUCTION OF SAME
Examiner	:	Zimmerman, John J.
Art Unit	:	1794
Confirmation No.	:	7228

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. §1.132

I, Yoichi Ikematsu, Ph.D., hereby declare and state as follows:

1. I am a co-inventor, along with K. Tanaka, S. Hayashi, H. Sawada, A. Takahashi, K. Honda, M. Suehiro, and Y. Takada of the above-identified patent application, which has been assigned to Nippon Steel Corporation ("Nippon"). I have been employed since 1988 by Nippon Steel Corporation, in Kanagawa, Japan at the Advance Technology Research Laboratories, R & D Bureau, engaged in analysis and evaluation of steel sheet material. I graduated in Material Engineering from Nagoya Institute of Technology in 1988 and obtained my doctorate in Engineering in 2000 from Tohoku University.

2. I have reviewed the Final Office Action mailed May 20, 2009, and the references cited therein, i.e., Japan No. 2001-323355 ("JP '355"), U.S. Patent No. 6,398,884 ("US '884"), and Japan No. 2000-290730 ("JP '730"). I have also reviewed pending claim 1.

3. I understand that the Examiner is of the opinion that JP '355 discloses a high strength galvanized steel having excellent corrosion resistance and platability wherein the

example compositions of the steel fall within the steel composition ranges required by Applicants' claim 1, and US '884 discloses a galvanized steel wherein the example compositions also fall within the claimed ranges for the constituents of the presently claimed steel (e.g. examples G-J in Table 1 of US '884). Further, JP '730 discloses a high strength galvanized steel having an excellent balance of strength and ductility wherein the example compositions of the steel fall within the claimed ranges for the constituents of the presently claimed steel (e.g. examples 1-13 in Table 1 of JP '730).

4. An experiment (Experiment 0) based on the conditions described in the present application (U.S. Application No. 10/552,668) was carried out. Experiment 0 was carried out according to the following procedure:

(a). The steel sheet composition contained (in mass%): 0.1% of C, 1.2% of Si, 1.1% of Mn, 0.3% of Al, 0.8% of Ni and 0.2% of Cu and a balance of Fe and unavoidable impurities.

(b). Steel sheet thickness: 0.8 mm.

(c). The steel sheet was heat treated using hot-dip glavanizing experimental facility in the following atmosphere: 10 mass% H_2 was added to N_2 gas introducing steam, and the ratio of PH_2O/PH_2 (the steam partial pressure and hydrogen partial pressure) was adjusted by controlling the amount of steam introduced. The steel sheet was heated to 800°C at a heating rate of 5°C/sec, this temperature was maintained for 100 sec., then cooled to room temperature at a cooling rate of 10°C/sec.

A film (with a thickness of 0.1 μm) of the steel sheet was observed by TEM observation working equipment with an acceleration voltage of 200 kV. The attached **Figure 1** shows a cross-sectional TEM image of a surface of the steel sheet. The image in **Figure 1** clearly shows that the internal oxide particles are formed near the surface of the steel sheet. The region identified as the internal oxide particle layer was evaluated using picture processing software equipped with the composition analysis device of TEM. Then image binarization was carried out in that same region. Next, each area of the particles was evaluated and converted to a circle equivalent diameter for which an average diameter of the particle was also determined. As a result, the average diameter of the internal oxide particle formed on the surface of the heat treated steel sheet was determined to be about 0.15 μm (as shown in the attached **Figure 2**).

5.   An experiment (Experiment 1) based on the conditions described in JP '355 was carried out. Experiment 1 was carried out according to the following procedure:

(a). The steel sheet contained (in mass%) 1.5% Si - 1.6 % Mn.

(b). The steel sheet was annealed at 780°C in an oxidation atmosphere with a combustion air ratio of 0.9, and reducing annealing was performed under an atmosphere of H_2: 5%, N_2: 95%, H_2O/H_2 ratio of 2×10^{-3} in the reducing zone.

(c). Then hot-dip galvanizing was performed.

This experiment confirms that the Si oxide and Mn oxide in JP '355 were formed in layers internally as shown in the attached **Figure A**. For instance, the attached Fig. A shows oxide formation on the steel sheet according to Experiment 1:

[Pink color portion represents SiO_2

Blue color portion represents Mn-O

White color portion represent Mn-Si-O complex oxides]

This means that the oxide formed on the steel sheet of JP '355 clearly exists in layers at the interface between the steel sheet and the plated layer, and the internal oxide is grown by supplying oxygen during reduction of Fe oxide existing on the surface of the steel sheet. It is assumed that there is a low oxygen concentration area inside of the iron oxide layer when the iron oxide layer is reduced. In this low oxygen concentration area, Si and Mn are already oxidized , and thus the formed oxides are grown and formed on the internal oxide layer in layers. The process of JP '355 therefore does not teach or suggest suppressing the production of an external oxide layer on the surface of the steel sheet by promoting the formation of an internal oxide layer.

In addition, as evidenced by **Figure A**, the average diameter of the internal oxide particles (e.g. Mn-Si-O, Mn-O, and SiO_2) formed in the steel sheet of JP '355 is more than 1 μm.

6.   An experiment (Experiment 2) based on the conditions described in JP '730 was carried out, and the cross-sectional area of the plated steel sheet of JP '730 was observed. Experiment 2 was carried out according to the following procedure:

(a). The steel sheet contained Si: 1.2%, and Mn: 1.6%.

(b). The steel sheet was annealed in an atmosphere adjusted to PH_2O/PH_2 ratio: 0.1, H_2: 5%, N_2: 95%, at a temperature of 800°C for 60 sec. (These conditions follow the same conditions as those shown in Table 2 of JP '730).

(c). Pickling was not performed for this experiment.

(d). The steel sheet was further annealed in an atmosphere adjusted to PH_2O/PH_2 ratio: 2×10^{-3}, H_2: 5%, N_2: 95% at a temperature of 800°C for 60 sec., then the annealed steel sheet was cooled to 470°C, subjected to Zn plating in the Zn containing bath, and galvanized and annealed at a temperature of 450°C for 60 sec. (These conditions follow the same conditions as those shown in Table 3 of JP '730).

In this experiment, the surface of the steel sheet containing plating layer was polished and Si dispersion was observed by EPMA. According to the conditions described in JP '730, although the internal oxide layer is formed in the steel sheet, and oxide particles are not observed in the plated layer, as shown in the attached **Figure B**. Further, it is confirmed that the internal oxide layer having a thickness of several microns was formed in a film-like state. The oxides are not observed in the plated layer because the Zn dispersion is inhibited by the oxide layer, therefore oxide particles cannot be captured in the plated layer even if the alloying treatment is carried out. Based on this experiment, I have concluded the following:

(1). When the annealing atmosphere is adopted to the Formula (1) in the CAL annealing defined in JP '730, the dense internal oxide layer having several microns thickness is formed on the steel surface. On the other hand, when the annealing atmosphere is adopted outside the range of the Formula (1), the internal oxide layer does not form densely. (*See* paragraph [0007] of JP '730).

This internal oxide layer of JP '730 remains just before the zinc plating step, and this internal oxide layer prevents dispersion of the dissolved Si and Mn, which existed in the core portion, to the surface layer during CGL annealing. (*See* paragraph [0028] of JP '730).

(2). The surface concentrate, which is an easily oxidized element of condensed Si and Mn formed at annealing is removed in JP '730. (*See* paragraph [0042] of JP '730).

(3). For the atmosphere in the CGL annealing of JP '730, it is desirable that the atmosphere is a fully reducing atmosphere for securing platability by means of reducing the oxide layer formed on the steel surface after pickling. (*See* paragraph [0042] of JP '730).

(4). In the JP '730, new oxide particles are not formed during CGL step because the CGL atmosphere during annealing has sufficient reduction atmosphere according to the range of Equation (2).

The internal layer formed in (1) above absorbs the dispersed Si and Mn from the inside of the steel sheet, and then the internal oxide layer is formed, after which the

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dissolved Si and Mn, which existed in the core portion, move from the internal oxide layer to the surface layer during CGL annealing. This is called as "Ostwald growth". Even if any oxide particles having a diameter of more than 0.01 µm and less than 1 µm (as defined in the present invention) were formed in the process of JP '730, the oxide particles formed would be energetically unstable, and disappear from the internal oxide layer due to Ostwald growth usually under the formation conditions of an internal oxide layer having several microns in thickness such that the oxide particles having a diameter of more than 0.01 µm and less than 1 µm are not observed with the steel product of '730.

7.   A cross-sectional view of a hot-rolled steel sheet with black skin scale (mill scale) is shown in the attached **Figure 9a** of US '884. The attached **Figure 9b** of US '884 shows a cross-sectional view of a cold-rolled steel sheet, and the attached **Figure 9c** of US '884 shows a cross-sectional view of a cold rolled steel annealed sheet. The black spots shown in **Figures 9a-c** appear to be the oxide particles and they are most visible in **Figure 9c**. As evidenced by **Figs. 9a-9c**, the average diameter of the internal oxide particles formed in the steel sheet of US '884 is more than 1 µm.

8.   Based on the above experiments and discussion, one of ordinary skill in the art following the disclosures of JP '355, US '884 and JP '730 would not have obtained the claimed high strength molten zinc plated steel sheet of the present invention. In particular, JP '355 does not suggest or teach suppressing the formation of an external oxide layer on the surface of the steel sheet and promoting the formation of an internal oxide layer inside the steel sheet in a reducing furnace in a continuous molten zinc plating system of the present invention. Whereas the internal oxide particles formed in JP '730 are energetically unstable, and disappear with Ostwald growth. We have also determined that the internal oxide particles formed in the steel sheet according to both JP '355 and US '884 have an average diameter of more than 1 µm.

*   *   *

I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title

18 of the United States Code, and that such willful false statements may jeopardize the validity of the patent or any reexamination certificate issued.

Respectfully submitted,

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Yoichi Ikematsu

_____
Date

Fig. 1 TEM image of the cross-sectional area of the steel sheet

Fig. 2 Binalized image of TEM image of the cross-sectional are of the steel sheet (extract the internal oxide particles)
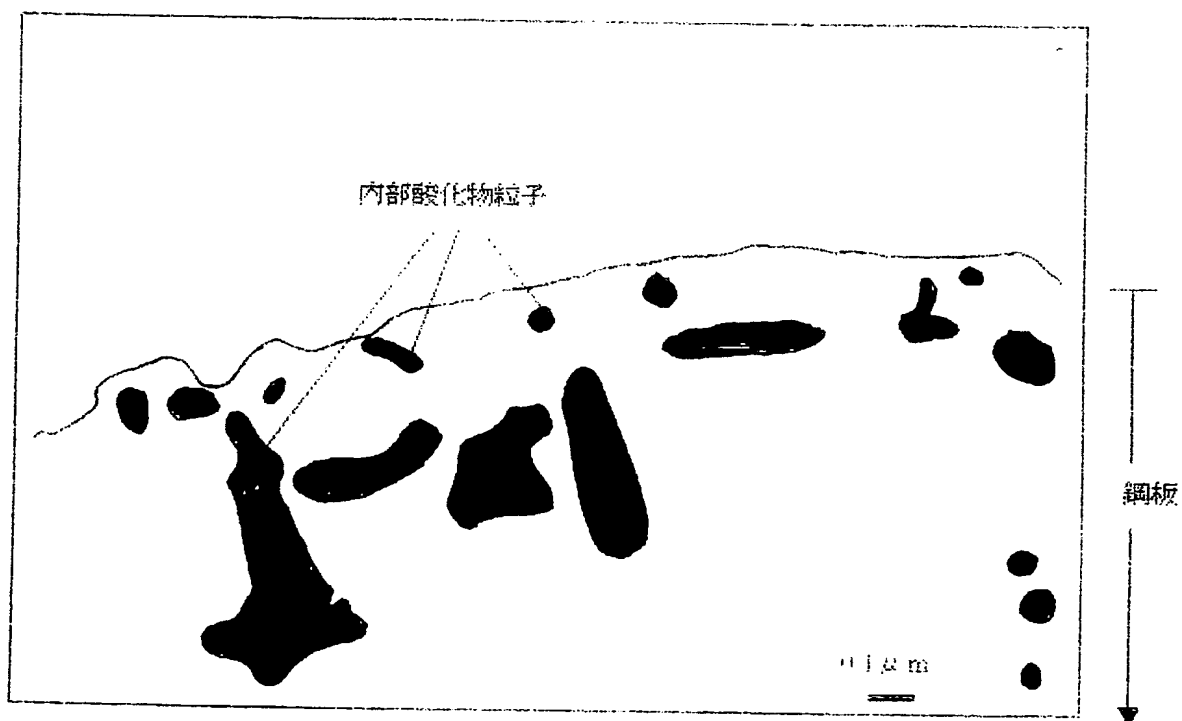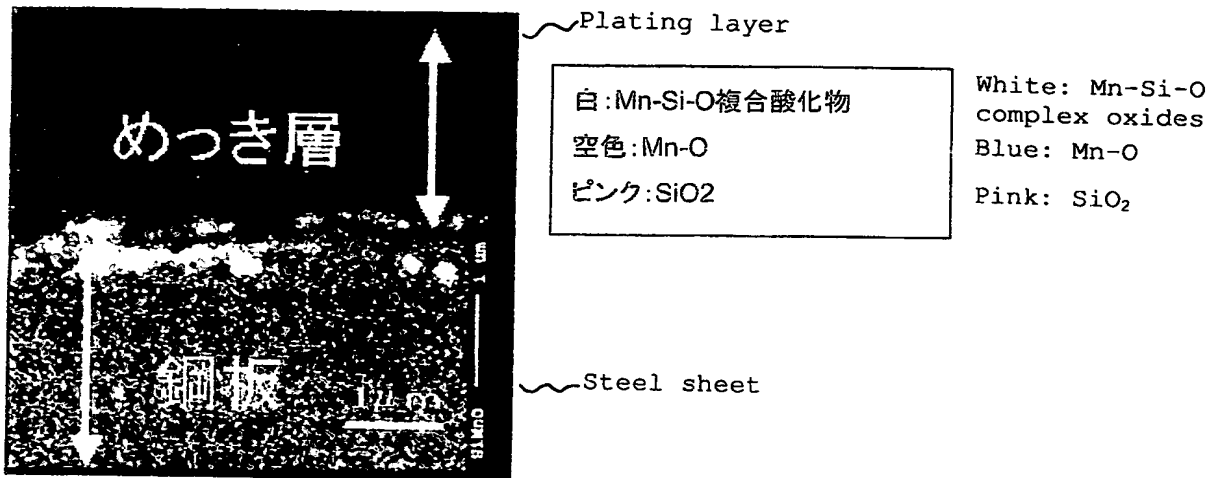
Fig. A

~Plating layer

白：Mn-Si-O複合酸化物
空色：Mn-O
ピンク：SiO2

White: Mn-S-O complex oxides
Blue: Mn-O
Pink: SiO₂

~Steel sheet

めっき層

鋼板　1μm

Fig. B

Siの状態

State of Si

酸化物　oxides

めっき層
Plating layer

鋼板
Steel sheet

Si　5 μm

酸化Si
Si oxide

鋼中に固溶または、めっき層中では0.1μm以下の酸化物

バックグラウンド
background

dissolved in the steel sheet or oxide having a dimeter of less than 0.1 μm in the plated layer

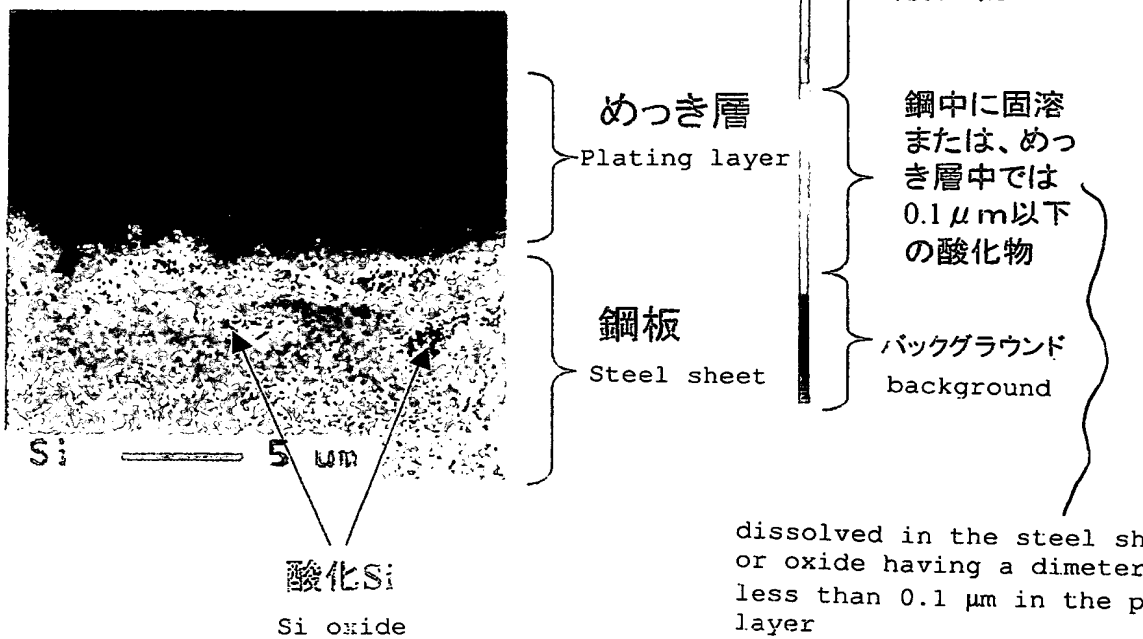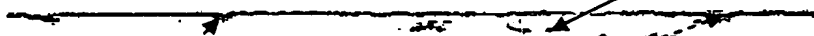## FIG. 9a

After heat treatment of hot rolled steel sheet
黒皮熱延板熱処理後 (800℃×10Hr) with black plain scale

FIG. 9b

After cold rolling
冷間圧延後

表層に露出
した酸化物

Oxides exposed on
the surface

酸化物
Oxides

FIG. 9c

冷間焼鈍後 (880℃×40s)

After annealing of the cold rolled steel sheet

10μm